

## Supporting Information for:

# Novel Molecular Design of "Graft" Assembly for Ordered Nanomorphology of P3HT-based Rod-Coil Copolymers

Hyeong Jun Kim,<sup>†</sup> Kwanyeol Paek,<sup>†</sup> Hyunseung Yang,<sup>†</sup> Chul-Hee Cho,<sup>†</sup> Jin-Seong Kim,<sup>†</sup>

Wonbo Lee<sup>‡</sup> and Bumjoon J. Kim<sup>\*†</sup>

<sup>†</sup>*Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 305-701, Korea*

<sup>‡</sup>*Department of Chemical and Biomolecular Engineering, Sogang University, Seoul 121-742, Korea*

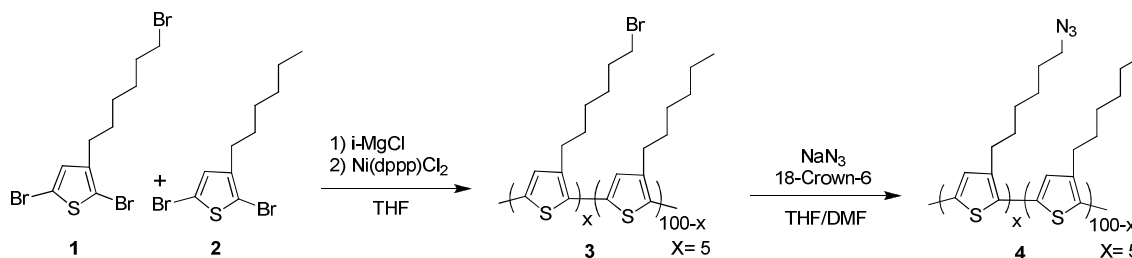
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\* E-mail: [bumjoonkim@kaist.ac.kr](mailto:bumjoonkim@kaist.ac.kr)

## Detailed Synthetic Procedure of P3HT-g-P2VP copolymers

**General:** Unless otherwise noted, commercially available reagents were used without further purifications. The progress of monomer reaction was checked with thin-layer chromatography (TLC) analysis using Merck silica gel 60 F254 pre-coated plates (0.25 mm) with a fluorescent indicator and was visualized with UV light (254 nm). Column chromatography was carried out on Merck silica gel 60 (230-400 mesh). All  $^1\text{H-NMR}$  spectra were recorded at 500 MHz, using  $\text{CDCl}_3$  as a solvent, unless otherwise stated. The chemical shifts of all  $^1\text{H-NMR}$  spectra are referenced to the residual signal of  $\text{CDCl}_3$  ( $\delta$  7.26 ppm) using Bruker 500 MHz NMR instrument. 2-vinylpyridine monomer was purified through vacuum distillation before the polymerization of P2VP-alkyne. 2,5-dibromo-3-(6-bromohexyl)thiophene (**1**) and 2,5-dibromo-3-(3-hexylthiophene) (**2**) were synthesized according to the previous methods.<sup>1-3</sup>

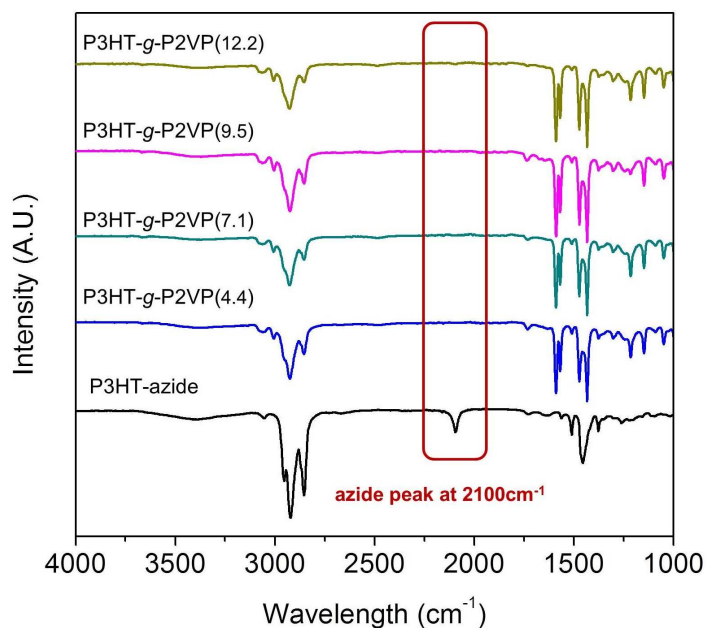


**Scheme S1.** Synthesis of azide-functionalized P3HT copolymers (P3HT-azide).

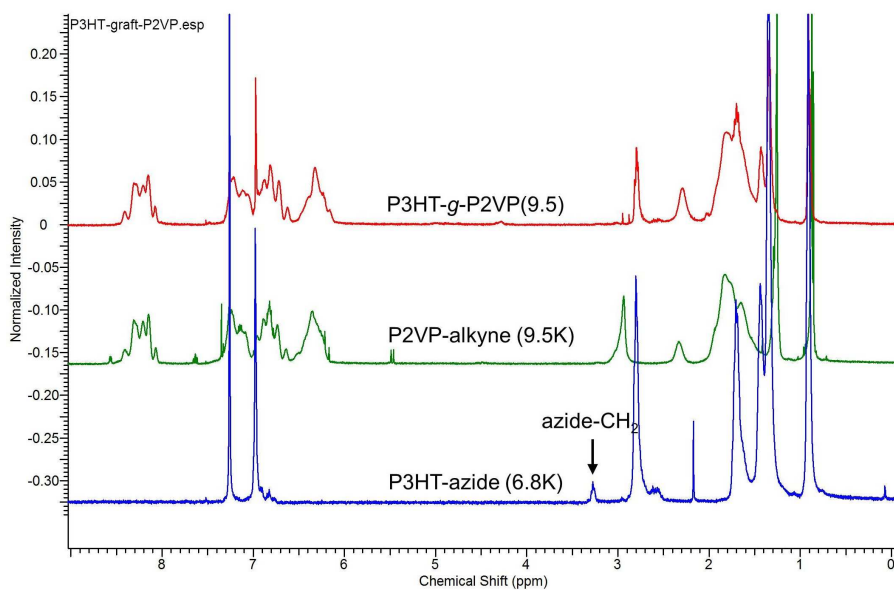
**P3HT-Br copolymer (3):** The mixture of 2,5-bromo-3-(6-bromohexyl)thiophene (**1**) (0.18 g, 0.45 mmol) and 2,5-dibromo-3-hexylthiophene (**2**) (2.82 g, 8.65 mmol) was placed in the flask under nitrogen atmosphere. Dry THF (40 ml) was added into the flask with a syringe, and the mixture was stirred at 0 °C. Then, Isopropyl-magnesium chloride (2.0 M solution in THF, 4.54 ml, 9.08 mmol)

was added, and the mixture was stirred at 0 °C for 1 h. Polymerization was initiated through addition of Ni(dppp)Cl<sub>2</sub> suspension (147 mg, 0.27 mmol) in dry THF to the mixture and polymerization was carried out at room temperature for 1 h. The polymerization solution was quenched with 2 mL of 1.0 M aq HCl to stop the polymerization. The synthesized polymer was precipitated with methanol (450 mL) containing 7 N NH<sub>3</sub> (6 mL) to neutralize acid, and the resulting precipitate was then filtered. Oligomers and impurities in the product were removed via Soxhlet extractions with methanol (6 h) and hexane (12 h), followed by chloroform extraction. The resulting solid was dried under vacuum to yield the product (**3**). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 6.98 (s, 1H), 3.42 (t, *J* = 6.5 Hz, BrCH<sub>2</sub>, 2H (5%)), 2.81 (t, *J* = 7.5 Hz, CH<sub>2</sub>, 2H), 1.65-1.76 (m, CH<sub>2</sub>, 2H), 1.40-1.50 (m, CH<sub>2</sub>, 2H), 1.26-1.40 (m, CH<sub>2</sub>CH<sub>2</sub>, 4H), 0.92 (t, *J* = 6.5 Hz, CH<sub>3</sub>, 3H (95%)).

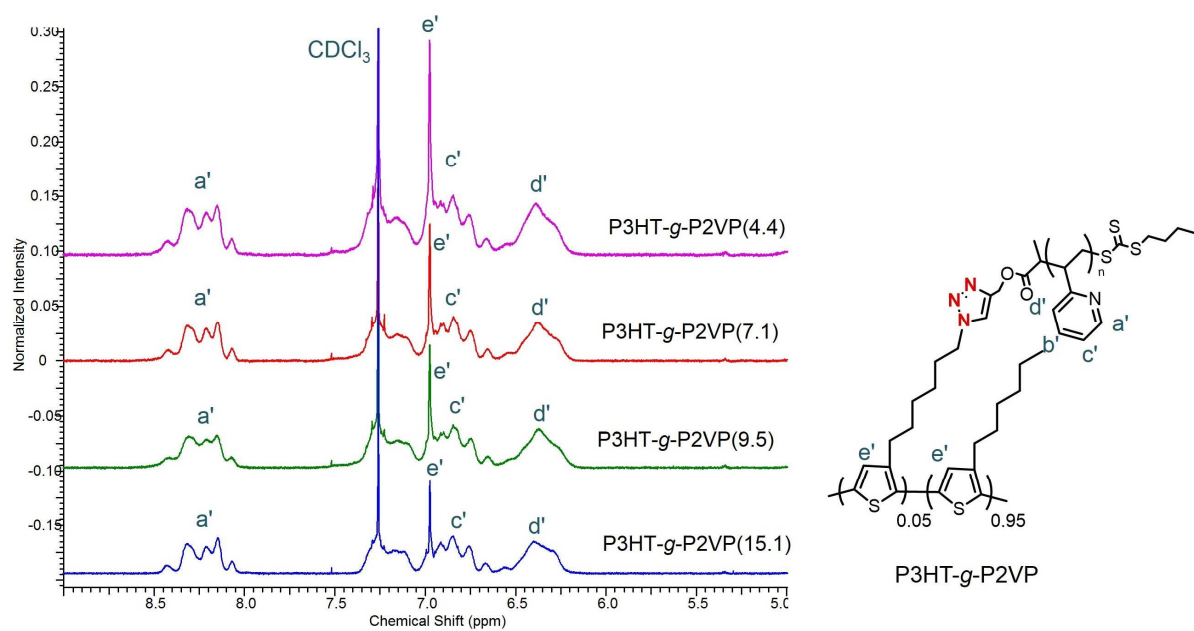
***P3HT-azide copolymer (4)***: P3HT-Br copolymer (**3**) (1.0 g) was dissolved in THF (40 mL). The NaN<sub>3</sub> (140 mg, 9.10 mol) and 18-crown-6 (567 mg 9.1 mol) was dissolved in DMF (10 mL) and sonication was applied to obtain homogeneous solution. DMF solution was added to P3HT-Br dissolved solution and then stirred at 40 °C for 8 h under nitrogen atmosphere. The polymer was precipitated with methanol and the resulting precipitate was then filtered. Residual NaN<sub>3</sub> was removed via Soxhlet extractions with methanol for 12 h. The resulting solid was dried under vacuum to yield the product (**4**). <sup>1</sup>H-NMR (500 MHz, CDCl<sub>3</sub>) δ 6.98 (s, 1H), 3.28 (t, *J* = 6.5 Hz, N<sub>3</sub>CH<sub>2</sub>, 2H (5%)), 2.81 (t, *J* = 7.5 Hz, CH<sub>2</sub>, 2H), 1.65-1.76 (m, CH<sub>2</sub>, 2H), 1.40-1.50 (m, CH<sub>2</sub>, 2H), 1.26-1.40 (m, CH<sub>2</sub>CH<sub>2</sub>, 4H), 0.92 (t, *J* = 6.5 Hz, CH<sub>3</sub>, 3H (95%)).



**Figure S1.** FT-IR curves for P3HT-azide and P3HT-g-P2VP copolymers. Strong peak at  $2100\text{ cm}^{-1}$  indicative of the presence of azide groups was found only in P3HT-azide. After the click reaction, the azide peak was not observed in the graft copolymers, indicating that there was no residual azide units after the microwave-assisted click reaction



**Figure S2.**  $^1\text{H}$ -NMR spectra for P3HT-azide, P2VP-alkyne ( $M_n = 9.5\text{K}$ ) and P3HT-g-P2VP(9.5). The azide- $\text{CH}_2$  peak of P3HT-azide at  $\delta = 3.28\text{ ppm}$  was totally disappeared after the click reaction



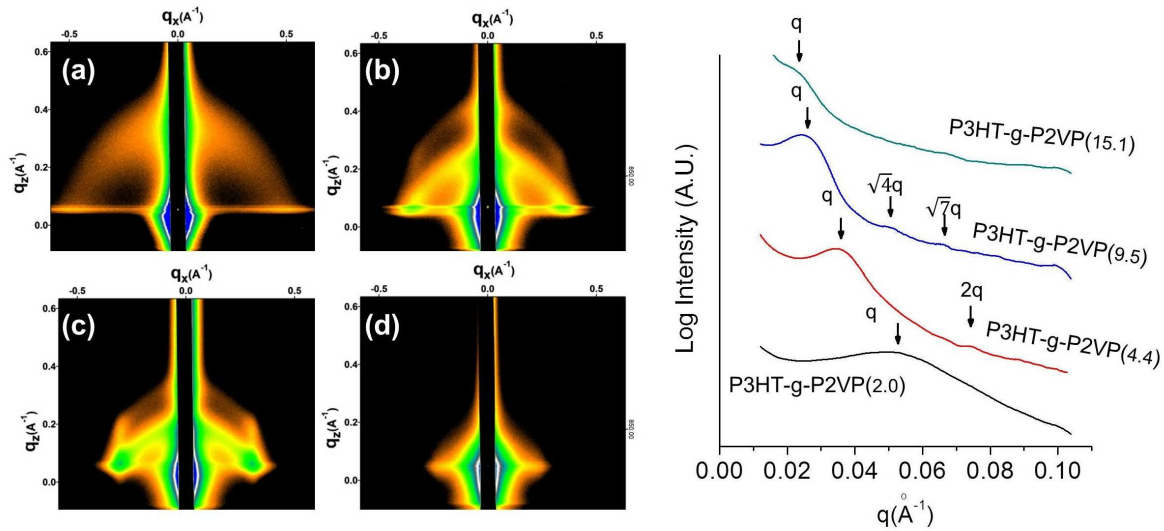
**Figure S3.**  $^1\text{H}$ -NMR spectra for the representative P3HT-*g*-P2VP copolymers with different  $M_{n,\text{P2VP}}$  values.

**Table S1.** Calculation of  $f_{\text{P3HT}}$  value of P3HT-*g*-P2VP copolymers from  $^1\text{H}$ -NMR spectra

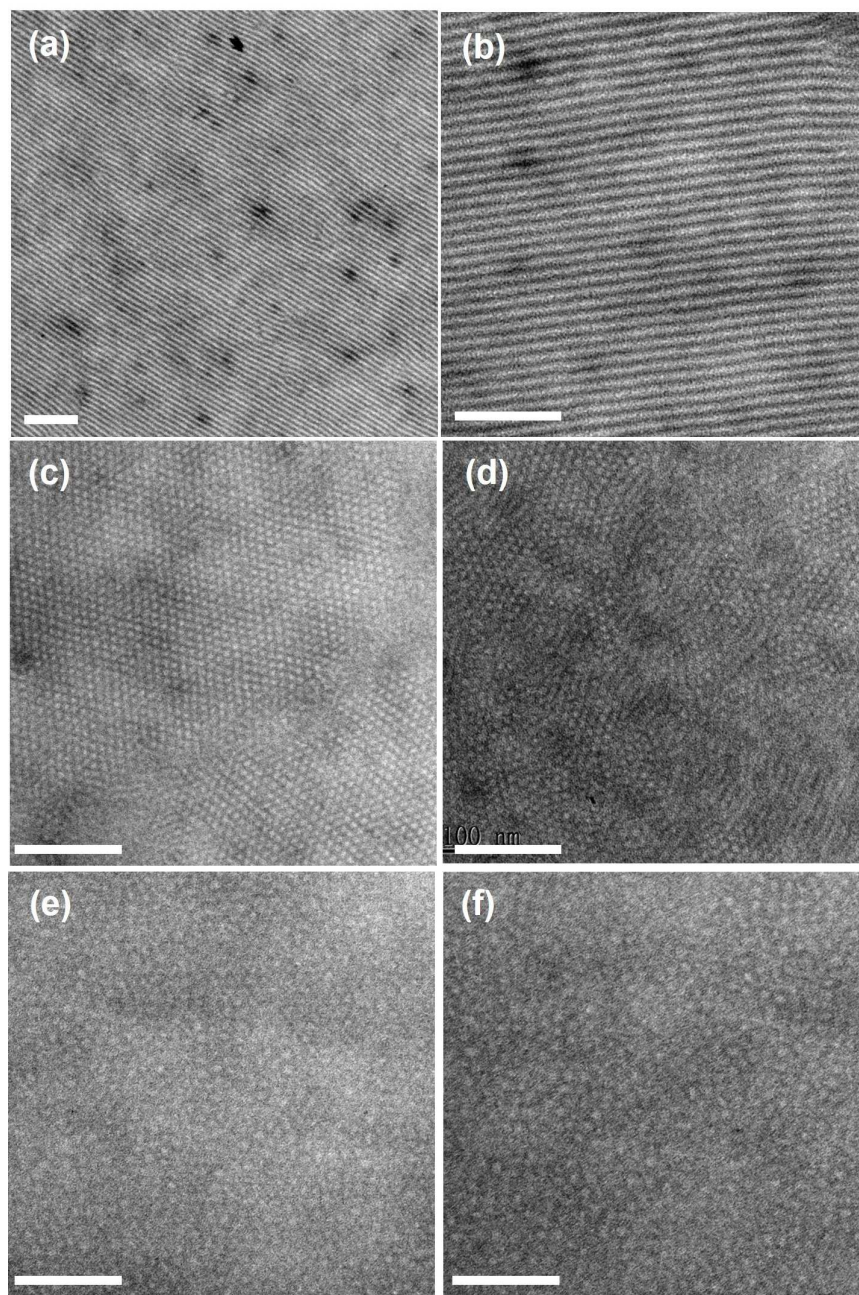
| Graft copolymer            | Integration of a' | Integration of c'+e' | Integration of d' | $f_{\text{P3HT, NMR}}^a$ | Calculated $M_{n,\text{P2VP}}^b$ [kg/mol] |
|----------------------------|-------------------|----------------------|-------------------|--------------------------|-------------------------------------------|
| P3HT- <i>g</i> -P2VP(2.0)  | 1                 | 2.08                 | 0.94              | 0.63                     | 2.02                                      |
| P3HT- <i>g</i> -P2VP(4.4)  | 1                 | 1.50                 | 1.01              | 0.45                     | 4.38                                      |
| P3HT- <i>g</i> -P2VP(7.1)  | 1                 | 1.31                 | 0.99              | 0.33                     | 7.06                                      |
| P3HT- <i>g</i> -P2VP(8.4)  | 1                 | 1.26                 | 0.95              | 0.29                     | 8.42                                      |
| P3HT- <i>g</i> -P2VP(9.5)  | 1                 | 1.23                 | 0.96              | 0.27                     | 9.52                                      |
| P3HT- <i>g</i> -P2VP(12.2) | 1                 | 1.18                 | 1.03              | 0.22                     | 12.17                                     |
| P3HT- <i>g</i> -P2VP(15.1) | 1                 | 1.15                 | 0.97              | 0.19                     | 15.08                                     |

$$^a f_{\text{P3HT}} = \{166.3 \times (I[\text{c}' + \text{e}'] - I[\text{a}']) / 1.10\} / \{166.3 \times (I[\text{c}' + \text{e}'] - I[\text{a}']) / 1.10 + 107.15 \times I[\text{a}'] / 1.14\}$$

$$^b f_{\text{P3HT}} = (M_{n,\text{P3HT}} / 1.10) / (M_{n,\text{P3HT}} / 1.10 + M_{n,\text{P2VP}} / 1.14)$$



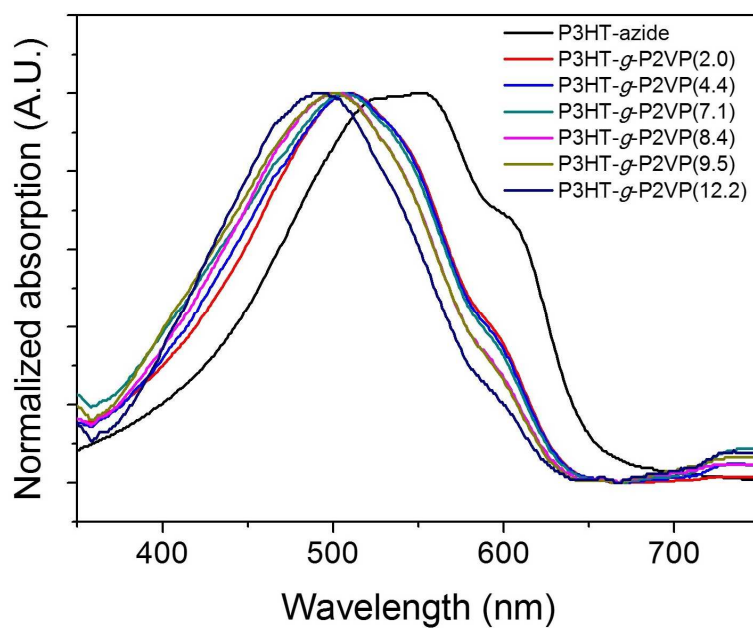
**Figure S4.** GI-SAXS patterns of (a) P3HT-g-P2VP(2.0), (b) P3HT-g-P2VP(4.4), (c) P3HT-g-P2VP(9.5) and (d) P3HT-g-P2VP(15.1). (e) In-plane cut ( $q_{xy}$ ) of GI-SAXS patterns for the representative P3HT-g-P2VP copolymers, each of four observed fibril, lamellae, hexagonally-packed cylinder and spheres.



**Figure S5.** Additional TEM images for (a),(b) P3HT-*g*-P2VP(4.4), (c)P3HT-*g*-P2VP(7.1), (d) P3HT-*g*-P2VP(8.4), (e) P3HT-*g*-P2VP(12.2) and (f) P3HT-*g*-P2VP(15.1). The scale bar is 200 nm.

**Table S2.** Thermal properties of P3HT-*g*-P2VP copolymer

| Graft copolymer            | $T_m$ [°C] | $T_c$ [°C] | $\Delta H_m$ [J/g] | Degrees of Crystallinity [%] |
|----------------------------|------------|------------|--------------------|------------------------------|
| P3HT-azide                 | 203        | 148        | 14.60              | 14.74                        |
| P3HT- <i>g</i> -P2VP(2.0)  | 188        | 137        | 8.07               | 8.15                         |
| P3HT- <i>g</i> -P2VP(4.4)  | 188        | 131        | 4.54               | 4.58                         |
| P3HT- <i>g</i> -P2VP(7.1)  | 187        | 118        | 2.42               | 2.44                         |
| P3HT- <i>g</i> -P2VP(8.4)  | 180        | 109        | 2.04               | 2.07                         |
| P3HT- <i>g</i> -P2VP(9.5)  | 176        | 105        | 1.80               | 1.81                         |
| P3HT- <i>g</i> -P2VP(12.2) | 177        | 116        | 1.72               | 1.73                         |
| P3HT- <i>g</i> -P2VP(15.1) | 180        | 112        | 1.62               | 1.64                         |

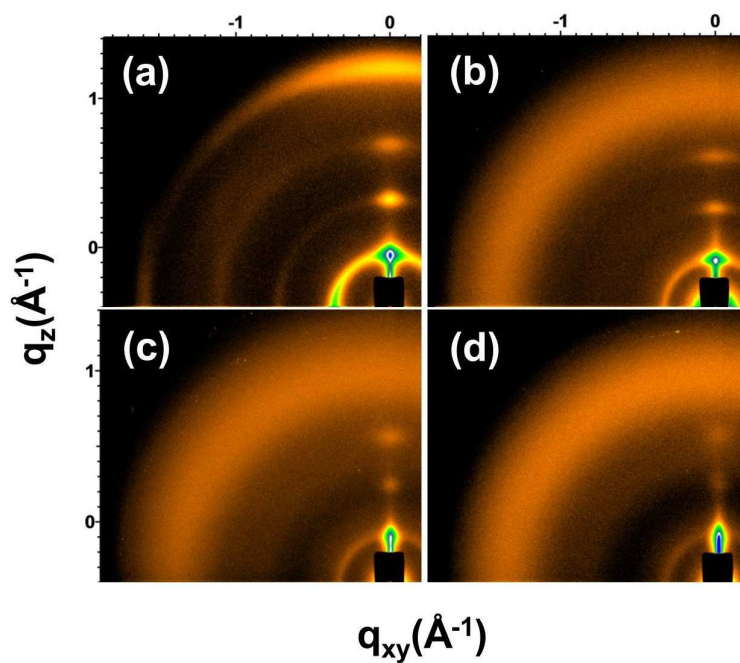


**Figure S6.** UV-vis absorption spectra of thin film of P3HT-azide and P3HT-*g*-P2VP copolymers

**Table S3.** Optical properties of P3HT-g-P2VP films

|                   | $\lambda_{\text{max}}$ | $I_{\text{vib}}/I_{\text{max}}^a$ |
|-------------------|------------------------|-----------------------------------|
| P3HT-azide        | 550 nm                 | 0.69                              |
| P3HT-g-P2VP(2.0)  | 511 nm                 | 0.35                              |
| P3HT-g-P2VP(4.4)  | 509 nm                 | 0.34                              |
| P3HT-g-P2VP(7.1)  | 506 nm                 | 0.32                              |
| P3HT-g-P2VP(8.4)  | 503 nm                 | 0.27                              |
| P3HT-g-P2VP(9.5)  | 501 nm                 | 0.25                              |
| P3HT-g-P2VP(12.2) | 493 nm                 | 0.19                              |

<sup>a</sup> ratio of relative intensity of the vibronic peak ( $I_{\text{vib}}$ ) at 600 nm to the maximum absorption peak ( $I_{\text{max}}$ )



**Figure S7.** GI-WAXS images for the P3HT-azide and representative P3HT-g-P2VP copolymers: (a) P3HT-azide, (b) P3HT-g-P2VP(2.0) ( $f_{\text{P3HT}}=0.63$ ), (c) P3HT-g-P2VP(4.4) ( $f_{\text{P3HT}}=0.45$ ), and (d) P3HT-g-P2VP(8.4) ( $f_{\text{P3HT}}=0.29$ ).

## References

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- (2) Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324.
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